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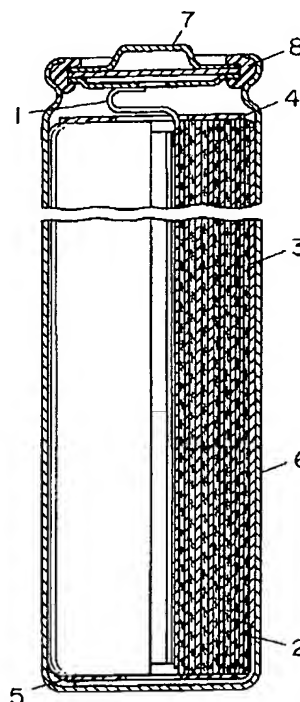
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(54)【発明の名称】 リチウム二次電池用正極活物質の製造方法およびリチウム二次電池

(57)【要約】

【課題】 優れた充放電特性を示すと共に、量産性の高い、リチウム二次電池用正極活物質の製造方法を提供する。

【解決手段】 一般式 $\text{LiNi}_{(1-x)}\text{Co}_y\text{M}_z\text{O}_2$ (ただし $0.1 \leq x \leq 0.3$, $0 \leq y \leq 0.3$, $0 \leq z \leq 0.3$, $x = y + z$ であり、MはAl, Mn, Mg, Fe, V, Ca, TiあるいはCrのうち少なくとも1種以上から成る) で表されるリチウム含有複合酸化物を、 $\text{Ni}_{(1-x)}\text{Co}_y\text{M}_z$ 水酸化物と水酸化リチウムの混合物を連続的に流動させながら水酸化リチウムの熔融温度以下で加熱し、脱水処理を行った後、静置して焼成することにより、嵩密度および混合度合いの向上した、優れた充放電特性を示すリチウム含有複合酸化物を、高い量産性で得ることができる。



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PATENT ABSTRACTS OF JAPAN

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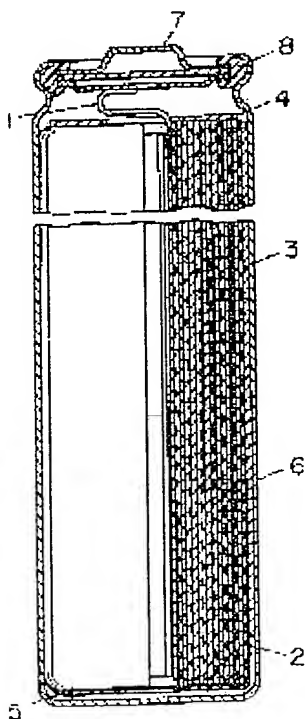
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(54) MANUFACTURE OF ACTIVE MATERIAL FOR LITHIUM SECONDARY BATTERY POSITIVE ELECTRODE AND LITHIUM SECONDARY BATTERY



(57)Abstract:

PROBLEM TO BE SOLVED: To manufacture a positive electrode active material for a lithium secondary battery showing excellent charging/discharging characteristics and offering a high mass-productivity.

SOLUTION: A lithium containing composite oxide expressed by $\text{LiNi}(1-x)\text{Co}_y\text{M}_z\text{O}_2$ (where $0.1 \leq x \leq 0.3$, $0 \leq y \leq 0.3$, $0 \leq z \leq 0.3$, and $x=y+z$, and M is one or more of Al, Mn, Mg, Fe, V, Ca, Ti, and Cr) is heated at a temp. below the melting point of lithium hydroxide while a mixture of $\text{Ni}(1-x)\text{Co}_y\text{M}_z$ hydroxides and lithium hydroxide is allowed to flow continuously, followed by a dehydration process and a baking process in stationarily placed condition. Thereby a lithium-containing composite oxide exhibiting excellent charging/ discharging characteristics and an enhanced bulk density and degree of mixing can be yielded with a high mass-productivity.

CLAIMS

[Claim(s)]

[Claim 1] General formula $\text{LiNi}_{1-x}\text{Co}_y\text{M}_z\text{O}_2$ (however, they are $0.1 \leq x \leq 0.3$, $0 \leq y \leq 0.3$, $0 \leq z \leq 0.3$, and $x=y+z$) In the manufacture approach of a lithium content multiple oxide expressed M -- the inside of aluminum, Mn, Mg, Fe, V, calcium, Ti, or Cr -- from at least one or more sorts -- changing -- The manufacture approach of the positive active material for lithium secondary batteries which compounds a lithium content multiple oxide by calcinating in the state of standing after heating below with the melting temperature of a lithium hydroxide and performing dehydration processing, making nickel $(1-x)$ Co_yM_z hydroxide and the mixture of a lithium hydroxide flow continuously.

[Claim 2] The manufacture approach of the positive active material for lithium secondary batteries according to claim 1 that the temperature of dehydration processing is 300 degrees C - 400 degrees C.

[Claim 3] The manufacture approach of the positive active material for lithium secondary batteries according to claim 1 that the temperature of baking is 700 degrees C - 900 degrees C.

[Claim 4] The lithium secondary battery characterized by coming to have the positive electrode using the lithium content multiple oxide compounded by one approach of claims 1-3 as positive active material, a negative electrode using the ingredient which carries out occlusion emission of the lithium, and nonaqueous electrolyte.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the lithium secondary battery using the manufacture approach of positive active material and it in a lithium secondary battery.

[0002]

[Description of the Prior Art] In recent years, portable-izing of consumer electronics and cordless-ization are progressing quickly, as these power sources, it is small and lightweight and the requests to the rechargeable battery which has a high energy consistency are mounting. The rechargeable lithium-ion battery attracts attention as a cell which has high density and high energy. Although a cobalt acid lithium is common as positive active material of a rechargeable lithium-ion battery, positive active material which changes to this from the problem of the resource of cobalt and the problem of cost is desired. For this reason, since a nickel acid lithium serves as low cost and high capacity compared with a cobalt acid lithium, that researches and developments are done briskly. However, composition of the nickel acid lithium which a charge-and-discharge property changes greatly with the synthetic approaches, and a nickel acid lithium shows a big charge-and-discharge capacity was made difficult.

[0003] However, in examination of synthetic conditions, the synthetic approach of a

nickel acid lithium which shows a big charge-and-discharge capacity is reported recently. For example, in order to make the approach (JP,5-290851,A) and homogeneity which compound a nickel acid lithium in a raw material calcinate nickel hydroxide and a lithium hydroxide, grinding mixing is carried out after the 1st baking, and in order to promote crystallization further, there is a method (JP,9-251854,A) of performing 2nd baking etc. [0004] Furthermore, in recent years, maintain the mixture of nickel hydroxide or basic nickel carbonate, and a lithium hydroxide 30 minutes or more in a temperature field 500 degrees C or less more than the melting temperature of the used lithium compound, the fused lithium compound is made to permeate into nickel oxide powder, and the method (JP,9-156931,A) of calcinating at the temperature of 650 more degrees C or more is indicated. By this approach, it is supposed that a nickel acid lithium can be cheaply manufactured by one baking.

[0005] Moreover, raising the engine performance of a nickel acid lithium further by other metals permuting the nickel metal of a nickel acid lithium, and raising a charge-and-discharge cycle (JP,8-222220,A) etc. is proposed.

[0006]

[Problem(s) to be Solved by the Invention] The mixture of the nickel hydroxide used as a start raw material at the time of compounding a nickel acid lithium and a lithium hydroxide is rich in hygroscopicity, and has the property which is easy to condense. Moreover, in order to compound the nickel acid lithium in which the outstanding charge-and-discharge property is shown, it is desirable to make a detailed lithium hydroxide into the source of a start, and the mixture itself becomes the low thing of bulk density from uniform contact of raw material fine particles being the need in a mixing stage inevitably.

[0007] When putting such mixture into a container, setting in the state of standing in an electric furnace and compounding a nickel acid lithium by baking once in a 450-900-degree C temperature requirement, in a synthetic process, an opening occurs in mixture with evaporation of the water of crystallization in a raw material. Therefore, contact of the particles of nickel hydroxide and a lithium hydroxide was bad, it became uneven synthetic reacting it, and there was a problem that a nickel acid lithium with a low charge-and-discharge property was compounded.

[0008] In order to solve this problem, there is the 2 times calcinating method for obtaining the lithium multiple oxide which was excellent in the charge-and-discharge property by performing grinding mixing after primary baking in the state of standing in a 300-650-degree C temperature requirement, attaining eburation between particles, and carrying out the second bake in a further 700-900-degree C temperature requirement. However, when beginning primary baking by standing, as mentioned above, since the bulk density of nickel hydroxide and lithium-hydroxide mixture is low, there are few amounts of mixture put in a container. Moreover, when a lot of mixture is put in and calcinated in a large-sized container, while dehydration processing takes time amount, a synthetic reaction also becomes uneven and a desirable cell property is not acquired. Furthermore, since the grinding mixing process after primary baking for obtaining the nickel acid lithium of the outstanding engine performance was needed, there was a problem that mass-production effectiveness was low.

[0009] Moreover, there is a method of manufacturing a nickel acid lithium cheaply by one baking by putting in the mixture of nickel hydroxide or basic nickel carbonate, and a lithium hydroxide in a batch type rotary kiln, maintaining 30 minutes or more in a

temperature field 500 degrees C or less more than the melting temperature of the used lithium compound, making the fused lithium compound permeate into nickel oxide powder, carrying out a temperature up further, and calcinating at the temperature of 650 degrees C or more.

[0010] However, by this approach, even if it once maintained to the temperature field 500 degrees C or less more than the melting temperature of a lithium compound, when it used above the melting temperature of a lithium compound, the iron and stainless steel which are generally used as a component of rotary kiln were corroded, and there was a problem of being unsuitable in prolonged use.

[0011] This invention solves such a technical problem, and it aims at offering the lithium secondary battery using the manufacture approach of the positive active material for lithium secondary batteries and it with high mass-production nature while it shows the outstanding charge-and-discharge property.

[0012]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, this invention is general formula $\text{LiNi}(1-x)\text{Co}_y\text{M}_z\text{O}_2$ (however, they are $0.1 \leq x \leq 0.3$, $0 \leq y \leq 0.3$, $0 \leq z \leq 0.3$, and $x=y+z$). In the manufacture approach of a lithium content multiple oxide expressed M -- the inside of aluminum, Mn, Mg, Fe, V, calcium, Ti, or Cr -- from at least one or more sorts -- changing -- After heating below with the melting temperature of a lithium hydroxide and performing dehydration processing, making nickel(1-x) Co_yM_z hydroxide and the mixture of a lithium hydroxide flow continuously, a lithium content multiple oxide is compounded by calcinating in the state of standing. The lithium content multiple oxide in which the outstanding charge-and-discharge property is shown is obtained by high mass-production nature by heating below with the melting temperature of a lithium hydroxide by performing dehydration processing of the water of crystallization of mixture, obtaining the mixture bulk density and whose mixed degree improved, and subsequently performing baking once in the state of standing, making mixture flow continuously.

[0013] Furthermore, this invention offers the lithium secondary battery which is equipped with the positive electrode using the lithium content multiple oxide compounded by the above-mentioned approach, the negative electrode using the ingredient which carries out occlusion emission of the lithium, and nonaqueous electrolyte, and changes.

[0014]

[Embodiment of the Invention] This invention is general formula $\text{LiNi}(1-x)\text{Co}_y\text{M}_z\text{O}_2$ (however, they are $0.1 \leq x \leq 0.3$, $0 \leq y \leq 0.3$, $0 \leq z \leq 0.3$, and $x=y+z$). In the manufacture approach of a lithium content multiple oxide expressed M -- the inside of aluminum, Mn, Mg, Fe, V, calcium, Ti, or Cr -- from at least one or more sorts -- changing -- After heating below with the melting temperature of a lithium hydroxide and performing dehydration processing, making nickel(1-x) Co_yM_z hydroxide and the mixture of a lithium hydroxide flow continuously, a lithium content multiple oxide is compounded by calcinating in the state of standing.

[0015] The effectiveness acquired by [this] performing dehydration processing is as follows, making it flow continuously. The fine-particles particle of mixture can be heated to homogeneity, evaporation of water of crystallization can be urged quickly, and dehydration processing can be ended completely in a short time. Moreover, since particles collide by flow and it is ground, the operation which makes contact of particles

dense is produced and the grinding mixing process before performing baking in the standing condition can be skipped. Furthermore, since a flow and mixing advance to coincidence while the water of crystallization in a mixture particle evaporates, improvement in bulk density and a mixed degree can be aimed at.

[0016] Here, especially as equipment heated while making it flow continuously, although not limited, when mass-production nature is taken into consideration, the continuous system rotary kiln equipped with continuation supply of mixture and a discharge device is desirable. Dehydration processing is carried out using this rotary kiln, and mass-production effectiveness improves twice [about] compared with the conventional 2 times calcinating method (manufacturing method which performs the primary baking-grinding mixing-second bake) by calcinating without grinding mixing once the mixture bulk density and whose mixed degree improved in the state of standing the middle.

[0017] Although it is necessary to heat the processing temperature in dehydration down stream processing below with the melting temperature (for melting to be started more at 410-420 degrees C of low temperature by the difference among conditions although a reference value is 445 degrees C) of the lithium hydroxide which is a raw material, since long duration is taken to finish dehydration, mass-production effectiveness worsens at less than 300 degrees C. Moreover, since the iron and stainless steel which are generally used as a component of rotary kiln are corroded above the melting temperature of a lithium hydroxide, it is desirable to carry out at 300 degrees C - 400 degrees C.

[0018] It becomes the structure with which the lithium went into the nickel part of a lithium content multiple oxide, and nickel went into the lithium part, respectively when discharge capacity became small since the crystallinity of a lithium content multiple oxide became low at less than 700 degrees C on the other hand as for the temperature of baking, and 900 degrees C was exceeded, the crystal structure changes to rock salt type structure from a hexagonal mold, and discharge capacity becomes small. These things to burning temperature has 700 degrees C - desirable 900 degrees C.

[0019] This invention is a lithium secondary battery which comes to have the positive electrode using the lithium content multiple oxide compounded by the above-mentioned approach as positive active material, a negative electrode using the ingredient which carries out occlusion emission of the lithium, and nonaqueous electrolyte.

[0020] the case where a positive electrode is produced using the lithium content multiple oxide by this invention as positive active material -- a lithium content multiple oxide, an electrical conducting material, and binder resin -- in addition -- further -- solvents, such as a formamide and N-methyl pyrrolidone, -- adding -- a paste-like positive electrode -- a mixture can be adjusted and it can produce by applying it to a positive-electrode charge collector, and drying.

[0021] The positive electrode formed from the positive active material mentioned above can be preferably used, when it constitutes the lithium secondary battery equipped with the negative electrode which consists of an ingredient which can occlusion emit a lithium, for example, a carbonaceous ingredient, a lithium alloy, etc., and the nonaqueous electrolyte which comes to dissolve lithium salt.

[0022] As an ingredient used as a negative-electrode active material of this lithium secondary battery, polymers, such as carbonaceous ingredients, such as pyrolytic carbon, corks, graphite, glassy carbon, an organic high molecular compound baking object, a carbon fiber, and activated carbon, or polyacethylene, and polypyrrole, etc. can be used,

for example. Moreover, for example, a lithium-aluminium alloy etc. can be used as a lithium alloy.

[0023] Nonaqueous electrolyte and the solid electrolyte which dissolve or distribute and become the same nonaqueous medium (a non-aqueous solvent or ion conductive polymer) as usual about a lithium salt electrolyte as the electrolytic solution can be used. For example, as a non-aqueous solvent of nonaqueous electrolyte, propylene carbonate, ethylene carbonate, ethyl MECHIRUKA-BONE-TO, butylene carbonate, vinylene carbonate, gamma-butyl lactone, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, 2-methyl tetrahydrofuran, methyl propionate, dimethyl carbonate, diethyl carbonate, JIPUROPIRUKA-BONE-TO, etc. can be used combining one sort or two sorts or more.

[0024] It is desirable on the property of a cell especially to be able to use LiClO_4 , LiPF_6 , LiAsF_6 , LiBF_4 , LiCF_3SO_3 , and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ grade, for example, among these to use LiPF_6 and LiBF_4 as an electrolyte dissolved in a non-aqueous solvent.

[0025] In addition, about other components of a lithium secondary battery, for example, a separator, and a cell can, it can be made to be the same as that of the conventional lithium cell, and especially, it is not limited and can be made various configurations, such as cylindrical, a square shape, a coin mold, and a carbon button mold.

[0026]

[Example] Hereafter, the nickel (example 1)-cobalt hydroxide ($\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$) what was expressed with 2 and coprecipitated the hydroxide of cobalt in nickel hydroxide) and lithium hydroxide ($\text{LiOH}\cdot\text{H}_2\text{O}$) explaining the example of this invention were mixed so that the atomic ratio of a lithium, nickel, and cobalt might be set to 1.0:0.8:0.2. Putting this mixture into the rotary kiln of volume 20L, and making it rotate by rotational frequency 2rpm, under the air ambient atmosphere of ventilation 10 L/min, to 350 degrees C, the temperature up was carried out and it held by the programming rate of 5 degrees C / min for 5 hours. Next, this mixture was put into the container made from an alumina, it put into the electric furnace of the oxygen ambient atmosphere which supplies oxygen by 10 L/min, the temperature up was carried out to 800 degrees C by the programming rate of 5 degrees C / min, and the lithium content multiple oxide ($\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$) was compounded by holding to this temperature for 15 hours. The obtained compound was ground and classified and it considered as the active material for cells.

[0027] Let the compound obtained by this composition be an active material 1. The positive-electrode plate was produced using the active material 1, and the cylindrical cell of the structure shown in drawing 1 was assembled. If the structure of this cell is explained, the group of electrode 3 which wound the positive-electrode plate and the negative-electrode plate spirally through the separator in the cell case 6 made from stainless steel arranges electric insulating plates 4 and 5 up and down, and is contained. The assembly obturation plate 7 and the insulating packing 8 which have a relief valve obturate opening of a case 6. A positive-electrode plate and a negative-electrode plate are the followings, and were made and produced.

[0028] N-methyl pyrrolidone solution which dissolved 4 weight sections and the polyvinylidene fluoride 4 weight section of a binder for the acetylene black of an electric conduction agent was added and kneaded to the lithium content multiple oxide 100 weight section, and it was made the shape of a paste. It ****(ed) to both sides of aluminium foil, and after desiccation, this paste was rolled out and used as the positive-

electrode plate with the thickness of 0.144mm, a width of face [of 37mm], and a die length of 250mm.

[0029] On the other hand, the negative electrode used what graphitized the mesophase microsphere (a mesophase graphite is called below). Styrene / butadiene rubber 3 weight section was mixed as a binder in this mesophase graphite 100 weight section, the carboxymethyl-cellulose water solution was added and kneaded, and it was made the shape of a paste. And coating of this paste was carried out to both sides of copper foil, and after desiccation, it rolled out and considered as the negative-electrode plate with the thickness of 0.21mm, a width of face [of 39mm], and a die length of 280mm.

[0030] And the lead made from nickel was attached in the product made from aluminum, and the negative-electrode plate at the positive-electrode plate, respectively, and it contained in the cell case with winding, a diameter [of 14.0mm], and a height of 50mm spirally through the separator with the thickness of 0.025mm, a width of face [of 45mm], and a die length of 740mm made from polyethylene.

[0031] What dissolved the 6 phosphorus-fluoride acid lithium of one mol / L in the solvent which mixed ethylene carbonate and ethyl methyl carbonate by the volume ratio of 20:80 was used for the electrolytic solution. It obturated and the cell 1 of an example took after pouring in this electrolytic solution.

[0032] (Example 1 of a comparison) A nickel-cobalt hydroxide ($\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$) and a lithium hydroxide ($\text{LiOH} \cdot \text{H}_2\text{O}$) same with having used in the example 1 were mixed so that the atomic ratio of a lithium, nickel, and cobalt might be set to 1.0:0.8:0.2, and it put into the container made from an alumina, and put into the electric furnace of the oxygen ambient atmosphere which supplies oxygen by 10 L/min, and the temperature up was carried out to 800 degrees C by the programming rate of 5 degrees C / min. The lithium content multiple oxide ($\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$) was compounded by holding to this temperature for 15 hours. The obtained compound was ground and classified and it considered as the active material for cells.

[0033] The positive-electrode plate was produced like the example 1 using this active material, and the cylindrical cell of the structure shown in an example 1 was assembled. Let this cell be the comparison cell 1.

[0034] (Example 2 of a comparison) A nickel-cobalt hydroxide ($\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$) and a lithium hydroxide ($\text{LiOH} \cdot \text{H}_2\text{O}$) same with having used in the example 1 were mixed so that the atomic ratio of a lithium, nickel, and cobalt might be set to 1.0:0.8:0.2, and it put into the container made from an alumina, and put into the electric furnace of the oxygen ambient atmosphere which supplies oxygen by 10 L/min, and the temperature up was carried out to 500 degrees C by the programming rate of 5 degrees C / min. It held to this temperature for 7 hours, and primary baking was performed.

[0035] After carrying out grinding mixing of the product after taken-out primary baking, it put into the alumina container again, and it put into the electric furnace in an oxygen ambient atmosphere, supplying the oxygen of 10 L/min as the second bake, and the temperature up was carried out to 800 degrees C by the programming rate of 5 degrees C / min. The lithium content multiple oxide ($\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$) was compounded by holding to this temperature for 15 hours. The obtained compound was ground and classified and it considered as the active material for cells.

[0036] The positive-electrode plate was produced like the example 1 using this active material, and the cylindrical cell of the structure shown in an example 1 was assembled.

Let this cell be the comparison cell 2.

[0037] (Example 3 of a comparison) A nickel-cobalt hydroxide ($\text{nickel}_{0.8}\text{Co}_{0.2}(\text{OH})_2$) and a lithium hydroxide ($\text{LiOH}\cdot\text{H}_2\text{O}$) same with having used in the example 1 were mixed so that the atomic ratio of a lithium, nickel, and cobalt might be set to 1.0:0.8:0.2. This mixture was put into the rotary kiln of volume 20L, and the temperature up was carried out to 800 degrees C by the programming rate of 5 degrees C / min under the oxygen ambient atmosphere which supplies oxygen by ventilation 10 L/min, making it rotate by rotational frequency 2rpm. However, the baking object fixed to the rotary kiln wall in the middle of the temperature up, and since it was checked that maintenance of a good baking condition cannot be performed, composition on this condition was stopped. Moreover, the wall of the rotary kiln after baking was violently corroded by the lithium hydroxide, and using a rotary kiln under an elevated temperature was checked when not realistic.

[0038] It examined on condition that the following using a cell 1 and the comparison cells 1 and 2. The constant current-constant-potential charge of 2 hours performed charge by 4.2V. The fixed limit resistance which a current value decreases was set up so that it might charge for a total of 2 hours, where it carried out 420mA constant-current charge until cell voltage amounted to 4.2V, and the load of 4.2V is carried out after that. Moreover, discharge carried out 610mA constant-current discharge, and the discharge beginning-and-the-end electrical potential difference was set to 3.0V. The charge and discharge of such conditions were performed under the 20-degree C environment, and discharge capacity of 5 cycle eye was made into initial capacity. The amount of specific volume of an active material was computed by having converted initial capacity into per 1g of active materials. Furthermore, what expressed the discharge capacity in the 500 cycle time to initial capacity with % was computed as a capacity maintenance factor.

[0039] The amount of active material specific volume of a cell 1 and the comparison cells 1 and 2 and a capacity maintenance factor are shown in Table 1.

[0040]

[Table 1]

	活物質比容量 (mA h / g)	容量維持率 (%)
電池 1	1 8 2	8 2
比較電池 1	1 7 1	6 7
比較電池 2	1 8 3	8 2

[0041] When the cell 1 was compared with the comparison cell 1 from Table 1, similarly to 800 degrees C the synthetic temperature at the time of a temperature up was not concerned, but it turned out that the amount of active material specific volume and capacity maintenance factor of the direction of a cell 1 are large.

[0042] This is considered that the synthetic reaction advanced to homogeneity by

calcinating, after aiming at improvement in a mixed degree while in the case of the positive active material of a cell 1 it performs dehydration processing, making the mixture of a lithium hydroxide and a nickel-cobalt hydroxide flow within rotary kiln and makes contact of particles dense.

[0043] On the other hand, in the positive active material of the comparison cell 1, as a result of put the mixture of a lithium hydroxide and a nickel-cobalt hydroxide into a container and compound by baking once, in a synthetic process, with evaporation of the water of crystallization in a raw material, an opening occur in mixture, a reaction serve as an ununiformity (the lithium content multiple oxide with which stoichiometric composition differ partially generate), and it be think that the amount of specific volume and the capacity maintenance factor fell.

[0044] On the other hand, although the amount of specific volume and the engine performance in which a capacity maintenance factor is equivalent to a cell 1 are obtained in the positive active material of the comparison cell 2 as a result of performing baking (primary baking-grinding mixing-second bake) twice, in respect of the mass-production nature of a lithium content multiple oxide, a cell 1 is not attained to far.

(Example 2) In this example, the temperature at the time of composition was changed to 650 degrees C - 950 degrees C, and the lithium content multiple oxide was produced. The synthesis method is explained below.

[0045] A nickel-cobalt hydroxide ($\text{nickel}_{0.8}\text{Co}_{0.2}(\text{OH})_2$) and a lithium hydroxide ($\text{LiOH}\cdot\text{H}_2\text{O}$) same with having used in the example 1 were mixed so that the atomic ratio of a lithium, nickel, and cobalt might be set to 1.0:0.8:0.2. Putting this mixture into the rotary kiln of volume 20L, and making it rotate by rotational frequency 2rpm, under the supplying-air air ambient atmosphere, to 350 degrees C, the temperature up was carried out and it held by the programming rate of 5 degrees C / min by ventilation 10 L/min for 5 hours. Next, this mixture was put into the container made from an alumina, it put into the electric furnace of an oxygen ambient atmosphere, supplying the oxygen of 10 L/min, and the temperature up was carried out to 650 degrees C - 950 degrees C shown in Table 2 by the programming rate of 5 degrees C / min, and the lithium content multiple oxide ($\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$) was compounded by holding after a temperature up for 15 hours. The obtained compounds 2-8 were ground and classified, and it considered as the active materials 2-8 for cells.

[0046] The positive-electrode plate was produced like the example 1 using these active materials 2-8, the cylindrical cell of the same structure as an example 1 was assembled, and it considered as cells 2-8. The charge and discharge test was performed for these cells on the same conditions as an example 1, and the amount of specific volume of an active material and the capacity maintenance factor in a 500 cycle time were computed.

[0047] The synthetic temperature of the active material used for cells 2-8 and the amount of active material specific volume, and a capacity maintenance factor are shown in Table 2.

[0048]

[Table 2]

	合成温度 (℃)	活物質比容量 (mA h / g)	容量維持率 (%)
電池 2	6 5 0	1 6 5	6 6
電池 3	7 0 0	1 7 8	7 5
電池 4	7 5 0	1 8 3	7 7
電池 5	8 0 0	1 8 2	8 2
電池 6	8 5 0	1 8 0	8 0
電池 7	9 0 0	1 7 2	7 1
電池 8	9 5 0	1 4 7	5 5

[0049] Table 2 showed that the amount of specific volume of an active material was good in the range whose synthetic temperature is 700 degrees C - 900 degrees C. Since the amount of active material specific volume of a cell and a capacity maintenance factor are high when especially synthetic temperature is 750 degrees C - 850 degrees C, it can be judged that composition at 750 degrees C - 850 degrees C is the the best for composition of a lithium content multiple oxide.

[0050] Here, it is considered because the crystal growth of a lithium content multiple oxide is inadequate that the amount of active material specific volume and a capacity maintenance factor will fall if synthetic temperature is lower than 700 degrees C. Moreover, it becomes the structure with which the lithium went into the metal part of a lithium content multiple oxide, and the metal went into the lithium part, a crystal structure changes from hexagonal mold structure to rock salt type structure, and it is considered to originate in barring diffusion of a lithium ion at the time of charge and discharge that the amount of active material specific volume and a capacity maintenance factor will fall remarkably if synthetic temperature exceeds 900 degrees C.

[0051] (Example 3) A nickel-cobalt hydroxide (nickel_{0.8}Co_{0.2} (OH)₂) and a lithium hydroxide (LiOH-H₂O) same with having used in the example 1 were mixed so that the atomic ratio of a lithium, nickel, and cobalt might be set to 1.0:0.8:0.2. Putting this mixture into the rotary kiln of volume 20L, and making it rotate by rotational frequency 2rpm, under the air ambient atmosphere which supplies air, to 350 degrees C, the temperature up was carried out and it held by the programming rate of 5 degrees C / min by ventilation 10 L/min for 5 hours. Let mixture processed here be mixture 1.

[0052] (Example 4 of a comparison) A nickel-cobalt hydroxide (nickel_{0.8}Co_{0.2} (OH)₂) and a lithium hydroxide (LiOH-H₂O) same with having used in the example 1 It mixed so that the atomic ratio of a lithium, nickel, and cobalt might be set to 1.0:0.8:0.2, and it put into the container made from an alumina, and put into the electric furnace of the air ambient atmosphere which supplies air by 10 L/min, the temperature up was carried out to 350 degrees C by the programming rate of 5 degrees C / min, and it held to this

temperature for 5 hours. Let mixture processed here be the comparison mixture 1.

[0053] The appearance bulk density (the weight of processed mixture is $\frac{W}{V}$ (g/cc) and computed in the deposition height of the mixture processed [container area-of-base x]) of the comparison mixture 1 in the example 4 of a comparison and the appearance bulk density (processed mixture is similarly computed from the deposition height when filling up the container of the same dimension as the example 4 of a comparison) of the mixture 1 in an example 3 are shown in Table 3.

[0054]

[Table 3]

	見かけ嵩密度 (g/cc)
混合物 1	0.91
比較混合物 1	0.51

[0055] The appearance bulk density of 0.91g [cc] /and the comparison mixture 1 of the appearance bulk density of mixture 1 was 0.51g/cc. Contact of the particles of mixture became [the direction which performed dehydration processing while making it flow continuously using rotary kiln] dense rather than having performed dehydration processing in the state of the usual standing, and it was checked that bulk density improves. The synthetic reaction in a subsequent standing condition can obtain the lithium content multiple oxide of the property which went on and was excellent in homogeneity from this by dehydration processing with rotary kiln.

[0056] In addition, it is not limited to the nickel-cobalt hydroxide (nickel_{0.8}Co_{0.2} (OH)₂) explained in the example as a start raw material, and this invention is nickel(1-x) CoyMz hydroxide (what carried out coprecipitation of cobalt and the hydroxide of M to nickel hydroxide.). M -- the inside of aluminum, Mn, Mg, Fe, V, calcium, Ti, and Cr -- from at least one or more sorts -- changing -- the same effectiveness can be acquired even if it uses.

[0057]

[Effect of the Invention] As mentioned above, making nickel(1-x) CoyMz hydroxide and the mixture of a lithium hydroxide flow continuously, according to this invention, by heating below with the melting temperature of a lithium hydroxide, dehydration processing of the water of crystallization of mixture is performed, and the mixture bulk density and whose mixed degree improved is obtained. Subsequently, while the charge-and-discharge property which was excellent by calcinating once in the state of standing is shown, the high lithium content multiple oxide of mass-production nature can be obtained.

Drawing 1

